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Vibrational quenching of NO$^+$(v) ions in collision with H$_2$, D$_2$, and O$_2$

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The vibrational quenching rate constants for NO$^+$(v), predominantly in the $v = 1$ state, have been measured at 200 and 293 K in collisions with H$_2$ and D$_2$ and at 200, 293, and 458 K with O$_2$. The rate constants are all very low, corresponding to quenching probabilities $\sim 10^{-4}$. The low rate constants reflect very shallow attractive potential wells. In the case of H$_2$ and D$_2$ this is a consequence of their low polarizabilities. In the case of O$_2$, repulsive chemical interactions offset the electrostatic attraction to yield a shallow attractive well. This is a consequence of the singlet NO$^+$ and triplet ground state O$_2$ not approaching on the attractive NO$_3^+$ ground state potential surface, which is a singlet. The temperature dependences of the quenching rate constants are generally slight, indicating that the collision energies are in a range comparable to the attractive well depth and that the quenching is not strongly dominated by either the attractive forces, which would give a negative energy dependence, or by the repulsive forces which would give a positive energy dependence.

I. INTRODUCTION

The application of the monitor ion technique to probe vibrational states of ions in selected ion flow drift tubes (SIFDT) has recently led to the systematic acquisition of vibrational quenching rate constants for diatomic positive ions, O$_2^+$(v),[1,2] NO$^+$(v),[3–5] HCl$^+$(v), and DCl$^+$(v).[6] In most cases the long range electrostatic attractive forces are large enough to dominate the deactivation process, as indicated by the large quenching efficiencies and their negative energy dependences.[7] A significant dipole moment for the quencher, or simply a polarizability as large as ~ 1.5 Å^3, yields an attractive electrostatic interaction large compared to kT which suffices for the attractive part of the potential to control the quenching.

The same situation sometimes occurs for neutral molecule vibrational quenching, i.e., large rate constants with negative energy dependences occur when chemical attractive forces exist. Examples are the hydrogen halide self-quenchings,[8] where hydrogen bonding provides the attractive interaction. Such attractive interactions, which are the usual case for ions and neutrals, are the exception in the case of neutral–neutral interactions.

When the attractive potential well depth is much less than the collision energy, usually $\sim 3/2\, kT$, the more usual case for neutral–neutral interactions, then quenching is dominated by the short range repulsive forces; under these conditions quenching is inefficient and increases with collision energy. The 300 K vibrational relaxation of N$_2$($v = 1$) requires $\sim 10^8$ collisions with N$_2$, and a similar large number with other small molecules (when resonant $V \rightarrow V$ transfer is not possible). This situation is well described by adiabatic-type collision theories and has been extensively treated by the Landau–Teller[9] theory and refinements of that theory.[8,10,11]

In the case of ion–neutral collisions, a weak electrostatic interaction is provided by neutrals with low polarizabilities such as helium, which is a very inefficient quencher of vibrationally excited ions.[1–4] The energy dependence of the rate constant for quenching (k_q) of N$_2^+$($v = 1$) by He[12] is described very well between 0.3 and 0.6 eV relative kinetic energy (KE) by a Landau–Teller, $\ln(k_q) \propto (\text{KE})^{-1/3}$, plot[13] yielding a repulsive interaction parameter in excellent agreement with theory.[14] A more exceptional case is that in which the normal electrostatic attraction is offset by chemical repulsion. This can only apply in cases where the ion and neutral correlate with a stable molecular ion so that chemical attractive and repulsive potentials arise. The only such case thus far identified experimentally is the quenching of NO$^+$($^1\Sigma$,v) by ground state O$_2$($^3\Sigma$). In this case, the collision partners approach NO$_3^+$ on a triplet state of an ion whose attractive ground state is evidently a singlet.[15] The present investigation establishes the rate constant for that quenching, previously known only as an upper limit.[5] The quenching of NO$^+$($^1\Sigma$,v) by O$_2$($^1\Delta$) has been found[15] to be extremely efficient, occurring at one-half the collision rate, presumably because the collision partners access the deep ground state attractive potential. It is possible, however, to make *a priori* predictions of very inefficient quenchings of ions when the potential curves are known to be repulsive, e.g., the vibrational quenching of NO$^+$($^1\Sigma$,v) ions by O(^3P) atoms must be slow since the lowest NO$_2^+$ triplet state is higher in energy than the reactants.

Since the collision energy is controllable (by varying temperature or ion velocity) it is possible to transit the relative kinetic energy range corresponding to the attractive potential well between the vibrationally excited species and the quencher. At energies below the well depth, long range at-

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tractive forces dominate, leading to a decreasing quenching rate constant with increasing energy, and at energies large compared to the well depth, short range repulsive forces dominate, leading to an increase in the quenching rate constant with increasing energy. Thus, one can expect to find minima in the quenching rate constants as a function of energy, broadly in the range of the attractive well depth.

Minima have been observed in the case of the hydrogen halide self-quenchings and for NO self-quenching.[8] Quenching of ions should, in principle, be easier to study since one can vary the relative kinetic energy more readily by applying an electric field in the SIFDT. However, to date only a few minima have been observed. One such case is the quenching of O_2^+ ($v = 1$) by Kr which shows a minimum, broadly in the range of the ~0.33 eV well depth.[16] This result has stimulated several theoretical analyses, including trajectory calculations, which reproduce the experimental behavior,[17,18] and more are in progress. Another such case is NO^+ (v) quenched by CH_4, where a broad minimum around 0.5 eV occurs.[19] The quenching of N_2^+ ($v = 1$) by He[12] appears to be approaching a minimum near zero electric field (3/2 kT~0.040 eV) roughly consistent with the theoretical 0.017 eV potential well.[14]

In cases where quenching is dominated by the attractive potential, the anisotropy of the potential is important.[7,18,20] One therefore expects rotational excitation to account for a significant fraction of the vibrational energy loss, and this is verified by trajectory calculations.[18] One also expects large dependences on both ion and neutral rotational constants in quenching, since the amount of rotational energy transferred for a given ΔJ increases with the rotational constant. In accord with this, the quenching of HCl^+ ($v = 1$) was found[6] to be faster than that of DCl^+ ($v = 1$) by Ar and Kr, and O_2^+ ($v = 1,2$) was found[2] to be quenched more efficiently by H_2 than D_2.

The present experiment provides a capability for measuring lower quenching rate constants than were accessible in the earlier experiments in Boulder[2] and Innsbruck,[3] where the lower limit was 10^{-12} cm^3 s^{-1}. The rate constants for quenching of NO^+ (v) by H_2, D_2, and O_2 studied here were all reported to be $< 10^{-12}$ cm^3 s^{-1} in the earlier studies.[3,4] The measurement of temperature dependences is also unique to the present experiment.

II. EXPERIMENTAL

The experiments were performed on the AFGL variable temperature selected ion flow drift tube. The apparatus has been described in detail[5] for measuring NO^+ vibrational quenching rates, and only details pertinent to the present experiment are given here. As detailed in a previous paper,[5] the relative vibrational populations of NO^+ (v) in the flow tube depend on the ion injection energy. In the present experiments, the ions were injected with 72 eV of kinetic energy in the laboratory frame. Under these conditions, 23% of the NO^+ ions are in $v > 0$ levels and less than 10% are in $v > 1$. The quenching rates are very small, so the sensitivity of the experiments had to be increased over the previous experiments. This was accomplished in several ways. The helium

velocity was reduced by throttling a butterfly valve in the exhaust line to the Roots blower. This decrease in the flow rate of the helium increased the reaction time and raised the pressure in the flow tube. The increase in pressure increased the number density of the quencher for a given flow rate of the quencher. Thus the increase in sensitivity was proportional to the square of the pressure increase. In addition, we added a flow controller with ten times the range of flow rates used previously. This allowed us to add much more quencher, approaching 10% of the buffer flow for the slowest quenching reactions.

The large quenchant flow rates used could have caused problems in the measurements. This was checked by doing the measurements in two ways. The majority of experiments were performed with a constant total pressure in the flow tube as the quencher was added. This was accomplished by the butterfly valve which was servocontrolled to the pressure as read by the capacitance manometer. In these experiments the flow rate down the tube changed slightly upon addition of large quencher flows since the total gas flow increased. The method used to check this was to keep both a constant flow of gas and a constant pressure. In this experiment, the helium flow was decreased proportionally to the added flow of the quenchant. The two methods gave the same results within 15%.

The slow quenching rates also required extreme caution with regard to the purity of the gases. We used ultrahigh purity gases (99.999% to 99.9999%). We also used several bottles of each gas to check for impurities and flushed our storage reservoir repeatedly. We continued the flushing process until at least three fillings yielded the same rate constant to within ± 20%, the experimental precision. We were unable to study quenching by H_2 and D_2 at high temperatures since the sensitivity of the experiment decreases with increasing temperature. We estimate the accuracy of the measurements to be ± 40% and the precision to be ± 20%. The accuracy quoted here is slightly less than the ± 30% accuracy normally reported[5] for measurements in the AFGL SIFDT apparatus, owing to the difficulties in the measurement of the small quenching rate constants for the reactions in this study.

III. RESULTS

The measured rate constants are given in Table I. A typical plot of the logarithm of NO^+ ($v > 0$) ion intensity as

TABLE I. Vibrational quenching rate constants k_q for NO^+ (v).

Neutral	k_q (cm^3 s^{-1})			k_c [a] $2\pi e\sqrt{\alpha/\mu}$ (cm^3 s^{-1})	Z(293 K) $= k_c/k_q$
	$T = 200$ K	$T = 293$ K	$T = 458$ K		
H_2	9.4(− 14)[b]	6.0(− 14)		1.5(− 9)	2.5(4)
D_2	5.7(− 14)	5.6(− 14)		1.1(− 9)	2.0(4)
O_2	2.3(− 13)	2.4(− 13)	1.9(− 13)	7.5(− 10)	3(3)

[a] k_c is the collision rate constant; e is electric charge of the ion; α is the polarizability of the neutral; μ is reduced mass.
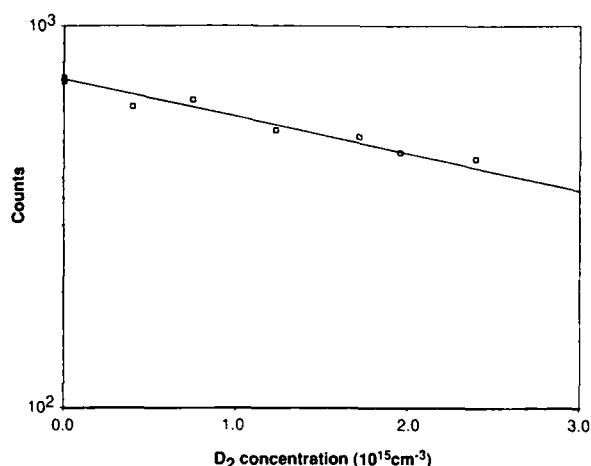[b] 9.4(− 14) = 9.4×10^{-14}.

FIG. 1. Experimental data for a typical decay of NO$^+$ ($v > 0$) ion counts as a function of added D$_2$ concentration. The solid line is a least squares fit to the data.

a function of added quenching gas D$_2$ is presented in Fig. 1. The important qualitative features of the data are:

(1) very inefficient quenching, requiring more than 10^3 collisions for O$_2$ and more than 10^4 for H$_2$ and D$_2$,

(2) weak or no temperature dependences,

(3) a small isotope effect.

The small quenching rate constants in each case imply that there cannot be very large attractive potentials. In every case so far studied with diatomic or polyatomic quenchers, attractive potentials as large as ~ 0.2 eV lead to $k_q > 10^{-12}$ cm^3 s^{-1}.[7,21] On the other hand, the quenching rate constants are too large to imply a purely repulsive potential for a vibrational frequency ($\bar{v}$) as high as that of NO$^+$, 2344 cm^{-1}. The 300 K vibrational quenching rate constant of N$_2^+$, $\bar{v} = 1876$ cm^{-1}, by He[12] is 5×10^{-15} cm^3 s^{-1} where the attractive well depth is 0.017 eV.[14] Thus the present results suggest attractive well depths $\gg 0.02$ eV and $\ll 0.2$ eV. In the case of H$_2$ and D$_2$ there is no chemical interaction and the electrostatic interaction is weak because the polarizabilities (α) of H$_2$ and D$_2$ are small ($\alpha \approx 0.8$ Å^3), leading to a small ion-induced dipole interaction ($-e^2\alpha/r^4$) where e is electric charge and r is interparticle distance. This polarizability is, however, greater than α(He) $= 0.2$ Å^3, consistent with more efficient quenching of ions by H$_2$ than by He.

The rate constants for quenching of O$_2^+$ (v) by H$_2$ and D$_2$ are substantially larger than those of NO$^+$ (v). The O$_2^+$–H$_2$ well depth is known to be < 0.2 eV.[22] The O$_2^+$–H$_2$ interaction is presumably stronger than the NO$^+$–H$_2$ interaction, since the vibrational quenching is so much faster, by a factor of 42 for H$_2$ and 12 for D$_2$ at 293 K. This probably reflects a "chemical" rather than electrostatic attraction associated with the fact that H$_2$O$_2^+$ (the hydrogen peroxide cation), is a chemically stable species, and perhaps aided by the fact that the ionization potential gap between O$_2$ and H$_2$ is less than that between NO and H$_2$, although the charge-transfer interaction is predicted to be very small in any case, ~ 0.1 eV.[21] Even a weak chemical interaction could provide the anisotropy of the potential which seems to be required to

explain the large H$_2$/D$_2$ isotope effect for the O$_2^+$ (v) quenching.[2] The NO$^+$–H$_2$ attractive interaction, being very weak and probably relatively isotropic, is consistent with the failure to find a significant H$_2$/D$_2$ isotope effect in the present studies.

When due allowance is made for the lower NO$^+$–D$_2$ collision frequency (Table I) due to the larger reduced mass, the relaxation efficiency for D$_2$ is slightly greater than that of H$_2$ at 293 K, and slightly less at 200 K. A possible explanation for the apparent temperature dependence of the isotope effect is that the relative attractive to repulsive interaction increases at lower temperature, and only attractive interactions are expected to depend on potential anisotropy (and lead to rotational excitation). However, this would strain the interpretation of the present data unacceptably, and we consider the isotope data inconclusive other than to support the weak attractive interaction indicated by the magnitudes of the quenching rate constants.

The small NO$^+$ (v)–O$_2$ quenching rate constant also implies a small attractive well. The rate constant, $\sim 2 \times 10^{-13}$ cm^3 s^{-1}, independent of temperature from 200–458 K, is too large to be due to a purely repulsive interaction and still very much smaller than typical quenching rate constants for neutrals with similar polarizabilities. For example, the quenching of NO$^+$ (v) by N$_2$, $k_q = 2.6 \times 10^{-12}$ cm^3 s^{-1}, is an order of magnitude faster,[5] whereas the polarizabilities of O$_2$(1.6 Å^3) and N$_2$ (1.7 Å^3) are similar. The NO$^+$·N$_2$ bond energy is known to be ~ 0.23 eV.[23] The O$_2^+$ ($v = 1$) quenching by N$_2$, with a similar bond energy ~ 0.21 eV,[23] has a rate constant, $k_q = 1.9 \times 10^{-12}$ cm^3 s^{-1}.[2]

The shallow NO$^+$·O$_2$ potential well deduced here is consistent with the slow three-body association of NO$^+$ with O$_2$. Previous measurements using an indirect technique have found the rate constant to be five times smaller than the association of NO$^+$ with N$_2$.[24] We have reinvestigated the NO$^+$ association with O$_2$ at 90 K and found no evidence for the association product, indicating an extremely slow rate. This implies that the NO$^+$·O$_2$ well depth is considerably less than the NO$^+$·N$_2$ well depth of 0.23 eV.

The potential surfaces of NO$_3^+$ for the lowest triplet state are not known and may be either attractive or repulsive. Even the heat of formation of ground state singlet NO$_3^+$ is not known, although it is clear from the O$_2$($^1\Delta$) quenching described above,[15] that it is a stable ion. Since the triplet curve is obviously not very attractive, from the present observations, the possibility exists that it is repulsive, and that a shallow potential well, $D \sim 0.1$ eV arises at large NO$^+$–O$_2$ separation due to an interplay between the long-range electrostatic attractive forces and the shorter range chemical repulsive forces. The nearest atom distance in NO$^+$–N$_2$ (in a nonlinear ON$^+$---N–N lowest energy configuration) is 2.6 Å[25] as a crude guide to what kind of distances might be expected.

The independence of k_q on temperature for NO$^+$ (v) quenching by H$_2$, D$_2$, and O$_2$ again implies a rough balance between the short range repulsive forces that would give a positive energy dependence and the long range attractive forces that would yield a negative energy dependence, i.e., a

relatively invariant potential over the translational energies involved, ~ 26 to ~ 60 meV, or perhaps as much as a factor of two or three larger than this. This range of temperature independent quenching rate constant is then analogous to the very broad minima observed in the kinetic energy dependences of the $O_2^+(v) + Kr$[16] and $NO^+(v) + CH_4$[19] quenching rate constants.

IV. CONCLUSIONS

The capability of measuring quite low vibrational collisional quenching rate constants has been demonstrated in the cases of $NO^+(v)$ quenching by H_2, D_2, and O_2. The small rate constants obtained, along with their weak temperature dependences and the small H_2/D_2 isotope effect are all consistent with shallow attractive potential wells in these interactions. The shallow wells in the H_2 and D_2 cases arise from the low polarizability of H_2; that in the NO^+–O_2 case is suggested to be due to offsetting long-range electrostatic attractions and short range electronic repulsion.

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